

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Bernard et al.

Serial No.: 09/630,517

Filed: August 02, 2000

For: POLYAMIDE NANOCOMPOSITES WITH OXYGEN SCAVENGING  
CAPABILITYCommissioner of Patents and Trademarks  
Washington, D.C. 20231

Group Art Unit: 1714

Examiner: K. I. Wyrozebski Lee

#10/8m  
06.27.02DECLARATION UNDER 37 CFR 1.131

We, Linda G. Bernard, Horst Clauberg, Michael J. Cyr, John W. Gilmer, James C. Matayabas, Jr., Jeffery T. Owens, Mark E. Stewart, Sam R. Turner, and Shriram Bagrodia declare that:

1. We are the coinventors of claims 1-29 of the above-identified patent application.
2. Prior to August 5, 1999, having earlier conceived the idea of recyclable polymer nanocomposite with improved oxygen and gas barrier properties comprising at least one polyamide resin, at least one oxygen-scavenging catalyst, and at least one layered silicate material, Linda G. Bernard, Jeffrey T. Owens, Marvin C. Hagey, and John W. Gilmer prepared the following polyamide polymer compositions, described herein, at the Research Laboratories of Eastman Chemical Co., Kingsport, Tennessee.
  - A) The following general procedures were used to measure oxygen consumption and carbon dioxide permeability. Oxygen consumption was measured on film samples, which were cut into strips, using a Columbus Instruments Micro-Oxymax respirometer with version 6.04b software. Samples were placed into a glass media bottle with a nominal volume of 250 mL. One empty bottle was included as a control blank. The bottles were attached to a ten port expansion module. Readings were taken at the start of the experiment and

then every four hours. The instrument measured the change in the oxygen concentration from the previous reading in each cell and calculated the total oxygen consumption and rate based on the (previously measured) volume of the cell plus oxygen sensor system. The oxygen sensor is an electrochemical fuel cell. Carbon dioxide transmission rates were measured on film samples using a Mocon permeability analyzer.

- B) An unmodified MXD6 polyamide was prepared by extruding two trilayer films comprising internal layers of about 10 and 30 vol% of unmodified MXD6 6007, available from Mitsubishi Gas Company, with two external layers of PET-9921, available from Eastman Chemical Company. Several 2-inch square sections of the trilayer films were stretched using a T. M. Long instrument (4x4 orientation at about 110°C). The carbon dioxide transmission rates were 174 and 59 cc(STP) CO<sub>2</sub>/meter<sup>2</sup>/24hr, for the 10 and 30 vol% films respectively.

A MXD6 polyamide composition containing about 4000 ppm cobalt acetate as an oxygen-scavenging catalyst was prepared by mixing 250 grams of a low molecular weight, amine terminated poly(m-xylylene adipamide), with IV of about 0.44 dL/g, and 4.23 grams of cobalt acetate tetrahydrate under a nitrogen atmosphere at 250°C for 120 minutes then cooling. X-ray analysis of the product showed the concentration of cobalt in the product to be about 4000 ppm. This cobalt-containing polyamide (10 parts) was extrusion compounded with 90 parts of MXD6 6007, available from Mitsubishi Gas Company, at 250°C, to give material with a cobalt concentration about 400 ppm. The polyamide was used to prepare trilayer films and 2-inch square sections of the films were stretched as described above. The carbon dioxide transmission rates of the oriented films were determined to be 168 and 54 cc(STP) CO<sub>2</sub>/meter<sup>2</sup>/24hr, for the 10 and 30 vol% films respectively. Oxygen consumption for 3.0 grams of the inner polyamide layer, after removing the PET 9921 layers from the unoriented film comprising 30 vol% polyamide, was determined to be about 370 microliters of oxygen over a period of 136 hours.

C) Using the procedure of example B, an MXD6 polyamide composition containing a layered silicate material and cobalt as an oxygen-scavenging catalyst was prepared by mixing 215.75 grams of a low molecular weight, amine terminated poly(m-xylylene adipamide), with IV of about 0.44 dL/g, 34.25 grams of SCPX-1578, an organoclay available from Southern Clay Products, and 4.23 grams of cobalt(II) acetate tetrahydrate under a nitrogen atmosphere at 250°C for 120 minutes followed by cooling. Ten parts of this product was extrusion compounded with 90 parts of MXD6 6007, available from Mitsubishi Gas Company at about 260°C to give material with a cobalt concentration of about 400 ppm and silicate concentration (ash) of about 1.0 wt%.

Two trilayer films were extruded comprising internal layers of about 10 and 30 vol% of the above compounded MXD6 6007 with two external layers of PET-9921, available from Eastman Chemical Company. Trilayer films were prepared and oriented as described above. The carbon dioxide transmission rates for the oriented films were 117 and 41 cc(STP) CO<sub>2</sub>/meter<sup>2</sup>/24hr, for the 10 and 30 vol% films respectively. Oxygen consumption for 3.0 grams of the inner nanocomposite layer, after removing the PET 9921 layers from the unoriented film comprising 30 vol% nanocomposite, was determined to be about 680 microliters of oxygen over a period of 136 hours.

D) Another MXD6 polyamide composition containing an oxygen-scavenging catalyst was prepared in which 4 parts of the MXD6 composite prepared in example B was extrusion compounded with 96 parts of amber PET-20261, available from Eastman Chemical Company. A trilayer film was extruded comprising internal layers of about 50 vol% of this material with two external layers of PET-9921, available from Eastman Chemical Company. Several 2-inch square sections of the trilayer films were prepared and oriented as above. The carbon dioxide transmissions rate of the oriented films were 411 cc(STP) CO<sub>2</sub>/meter<sup>2</sup>/24hr, for the 50 vol% films. Oxygen consumption for 10

grams of the unoriented film comprising 50 vol% of the extrudate of PET 9921 with the PET-polyamide composite was determined to be about 60 microliters of oxygen over a period of 136 hours.

- E) Another MXD6 polyamide composition containing a layered silicate material and an oxygen-scavenging catalyst was prepared in which 4 parts of the MXD6 composite prepared in example C was extrusion compounded with 96 parts of amber PET-20261, available from Eastman Chemical Company. Two trilayer films were extruded comprising internal layers of about 30 and 50 vol% of this material with two external layers of PET-9921, available from Eastman Chemical Company. Trilayer films were prepared and oriented as above. The carbon dioxide transmissions rates of the oriented films were determined to be 317 and 291 cc(STP) CO<sub>2</sub>/meter<sup>2</sup>/24hr, for the 30 and 50 vol% films respectively. Oxygen consumption for 10 grams of the unoriented film comprising 50 vol% of the extrudate of PET 9921 with the nanocomposite was determined to be about 60 microliters of oxygen over a period of 136 hours.
- F) A polyamide composition was prepared in which the oxygen-scavenging catalyst, cobalt, was intercalated into the polymer matrix through the layered silicate material. A Wyoming-type montmorillonite clay was prepared in which 50% of the sodium cations were exchanged with cobalt and 50% with protons. Ash content of the clay was 87.15 wt %, cobalt content was 1.23 %, and X-ray basal spacing was 1.25 nm. The treated clay was dry mixed with 269 parts of a low molecular weight poly(m-xylylene adipamide), with IV of about 0.41 dL/g. The mixture was dried at 110°C overnight in a vacuum oven then extruded. The extruded material showed good oxygen consumption.
- G) Another polyamide composition was prepared identically to E except the montmorillonite clay used in the composition had 50 % of the sodium cations are exchanged with cobalt(II), 25% with octadecyltrimethylammonium cations,

and 25 % with protons. The clay had a cobalt content of 0.99 %, and X-ray basal spacing of 1.34 nm. The extruded material showed good oxygen consumption.

3. Evidence supporting the above examples above are provided by copies of research notebook pages as set forth in the table below and attached hereto:

Experiment	Supporting Notebook Pages	Performed by
B	X-26645-100 X-26645-103 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
C	X-26645-101 X-26645-103 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
D	X-26645-103 X-26645-113 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
E	X-26645-101 X-26645-103 X-26645-113 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
F	X-26640-085 X-26854-015 X-25982-122	Marvin C. Hagey John W. Gilmer Jeffery T. Owens
G	X-26640-087 X-26854-015 X-25982-122	Marvin C. Hagey John W. Gilmer Jeffery T. Owen

Further evidence of the conception of one aspect of this invention is provided by page X-25982-100 from Mr. Owens notebook, also attached hereto.

4. Each of the dates deleted from the attached notebook pages is prior to August 5, 1999.

The undersigned declares further that all statements made herein on his own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with a knowledge that willful, false statements, and the like so made are punishable by fine, or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

June 10, 2002  
Date

Linda Gail Bernard  
Linda Gail Bernard

\_\_\_\_\_  
Date

\_\_\_\_\_  
Horst Clauberg

\_\_\_\_\_  
Date

\_\_\_\_\_  
Michael John Cyr

June 4, 2002  
Date

John Walker Gilmer  
John Walker Gilmer

June 4, 2002  
Date

\_\_\_\_\_  
James Christopher Matayabas, Jr.

June 4, 2002  
Date

Jeffery Todd Owens  
Jeffery Todd Owens

June 5, 2002  
Date

Mark Edward Stewart  
Mark Edward Stewart

June 5, 2002  
Date

Sam Richard Turner  
Sam Richard Turner

Docket: 71111

PATENT

June 10, 2002  
Date

Shriram Bagrodia  
Shriram Bagrodia

## Preparation of D(ND) 4000 PPM Cobalt

Objective: Prepare the above to be let down into MXD6 @ 400 PPM Cobalt  
 the Final material will be used as the center layer in multifiber film  
 and the goal is that the cobalt will act as an O<sub>2</sub> scavenger.

Preparation: The Following were weighed into a 34/45, single-neck, 1L, round-bottom Flask and heated until melted while stirring slowly under strong N<sub>2</sub> purge. When the material is removed from the N<sub>2</sub> saturated flask, it will be enclosed in a plastic bag to break up into pieces, placed in a glass (quart Kerr Jar) container and then placed in an oven @ 80°C under nitrogen.

RXNE	Grams Needed	Comments
D(ND)	250	Batch 96100261
Cobalt Acetate	4.23	Lot 4519 KEVP Mallinckrodt

Report: Reactor C Date: [REDACTED] Time: 15:17:51  
 Recipe Name: C:\CAMILETG\RECIPES\DND\_CO.RCP  
 Notebook Name: X26645-100  
 Flags: S=Stirrer Slaved, T=Service Traps, C=Add Catalyst

Stage	Time Min	Temp °C	Vac Torr	Stir RPM	Power %	Flags <input type="checkbox"/>	Estimated End Time
1	1	245	730	0	0	S T C	15:18:51
2	120	245*	730	250	0	0 0 0 0	17:18:51

\*I had to increase this temp. to 250°C to get the D(ND) to melt so the Cobalt could be stirred into the polyamide.

Note:  
 When I got ready to remove the polyamide from the polymer rig, I kept the flask under N<sub>2</sub> flow as long as I could, then I broke the flask quickly, broke the polyamide as best as I could using a cloth, plastic bag & a hammer. The chunks were not small enough; therefore, I placed the chunks in a quart Kerr jar & put it in the oven @ 80°C & a good N<sub>2</sub> flow. Later I removed the jar from the oven, sealed it & broke the chunks further with the polymer chopper. I will grind them tomorrow. lcf [REDACTED]

SIGNATURE OF AUTHOR Linda Bernard

SIGNATURE OF WITNESS Luttrell Williams

DATE [REDACTED]

DATE [REDACTED]



X 26645

No

101

Preparation of D(ND) / ~~20.0wt%~~ 10.0wt% SCPX-1578 / 4000 PPM Cobalt

Objective and Procedure: See P-100

RXN#	Grams Needed	Comments
D(ND)	215.75	Batch 96100261
SCPX-1578	34.25	Southern Clay Products
Cobalt Acetate	4.23	Lot 4519 KEVP Mallinckrodt

Report: Reactor D Date:  Time: 15:18:24  
 Recipe Name: C:\CAMILETG\RECIPES\DND\_CO.RCP  
 Notebook Name: X26645-101  
 Flags: S=Stirrer Slaved, T=Service Traps, C=Add Catalyst

Stage	Time Min	Temp °C	Vac Torr	Stir RPM	Power	Flags S T C	Estimated End Time
1	1	245	730	0	0	0 0 0	15:19:24
2	120	245*	730	250	0	0 0 0	17:19:24

\* I had to increase the temp of this run to 260°C to get the polyamide to melt and distribute the Cobalt + clay throughout the polyamide.

See note on P-100 for removal and chopping method. 1 lb

Analysis of 100 and 101: X-Ray      wt% Ash = 10.32%

100 = 4,000 PPM Cobalt or 0.40%  
 101 = 3,800 " " or 0.38%

TEC 8573-3

SIGNATURE OF AUTHOR

Linda Bernard

DATE

SIGNATURE OF WITNESS

Gustave Muller

DATE

X 26645

No 103

Submitted MXD6/D(ND)/CWC-ODA/Cobalt Samples For Compounding  
Objective: Compound the above @ 400 ppm Cobalt and 10 wt%  
Silicate to be used in tri-layer film extrusion to act as an  
oxygen scavenger.

Procedure: Mixed the following in 2-1/2 gallon jars.

Item 1 MXD6 1080g D(ND)/Cobalt 120g D(ND)/CWC-ODA/Cobalt 120g  
Reference = X26645-101  
Item 2 MXD6 1080g D(ND)/Cobalt 120g  
Reference = Grade 6007 Lot # S80106 Reference = X26645-101

Linda Bernard

Item	MXD6 Ref: Grade 6007 Lot # S10806	D(ND)/Cobalt Ref: X26645-100	D(ND)/CWC-ODA/Cobalt Ref: X26645-101	Total Grams
1	1080	120		1200
2	1080		120	1200

PAGE

BOOK

No 106

X 25036

Linda Bernard EXT. 8060 R12560  
X-26645-103 - 1,2

ZONE TEMP. SET PT. 1. 2. 3. 4. 5. 6. 7. 8.  
240 260 260 260 260 260 260 260  
103-1 ACTUAL 240 260 260 260 260 260 260 260  
103-2 ACTUAL 240 260 260 260 260 260 260 260

MELT P.S. MELT TEMP. TORQUE FEEDER ST. RPM  
103-1 170 253 72 7 250  
103-2 180 254 73 5 250

Item	MXD6 Ref: Grade 6007 Lot # S10806	D(ND)/Cobalt Ref: X26645-100	D(ND)/CWC-ODA/Cobalt Ref: X26645-101	Total Grams
1	1080	120		1200
2	1080		120	1200

SIGNATURE OF AUTHOR

DATE

SIGNATURE OF WITNESS

DATE

TEC 6573-4 (7-80)

TEC 6573-3

SIGNATURE OF AUTHOR

DATE

SIGNATURE OF WITNESS

DATE

X-Ray Analysis:

Item #1 = 476 ppm  
Cobalt

Item #2 = 441 ppm  
Cobalt

Retested by ICP

Ash Analysis:

Item #1 = 0.01 wt%

" #2 = 1.06 wt%

Retested by ICP

For ppm Co:

Item #1 = 396 ppm Co

" #2 = 320 ppm Co

**X 26645**

No

113

Submitted Cobalt Materials to be Compounded w/ PET 20261

Objective & Procedure : See P-003

Submitted on

Linda Bernard

### X-Ray Analysis:

Item # 1 = 16 ppm Co.

$$11 \quad \# 2 = 16 \quad " \quad "$$

№ 108

X 25036

Linda Bernard  
X 26645 - 113-1-2

### Ash Analysis:

Item #1 = 0 wt %

11 # 2 = 0.0516 wt% Ash

Temp Set	1	2	3	4	5	6	7	8
113-1	100	275	275	275	275	275	275	275
Actual	100	229	275	275	275	275	275	262

<u>Temp Set</u>								
.113-2	100	275	275	275	275	275	275	275
Actual	100	275	275	275	275	275	275	258

	Melt Press	Melt Temp	Torque	Feeding Set	R.P.M
113-1	190	246	85	3	315
113-2	200	241	75	3	315

Item	Reference of PET	Material Added	Reference of Co Additive	Grams of PET	Grams of Co Additive	Total Grams of Sample
1	Amber - 20261	MXD6/D(ND)/Cobalt	X26645-103-1	1920	80	2000
2	Amber - 20261	MXD6/D(ND)/SCPX-1578/Cobalt	X26645-103-2	1920	80	2000

SIGNATURE OF AUTHOR R. McConnell DATE [REDACTED] REC 6173-1 (2-66)

SIGNATURE OF WITNESS \_\_\_\_\_ DATE \_\_\_\_\_

TEC 6573-3 (2-88)

SIGNATURE OF AUTHOR

SIGNATURE OF WITNESS

DA

DATE \_\_\_\_\_

X 26645

No 117

Submitted Samples to David Jessee To Be Used in Tri Layer Film Extrusion

Objective: Determine How Effective the Materials are in enhancing Barrier Properties and Adhesion of the Layers Containing AQ48.

Procedure: Submitted the Samples VIA B-125's electronic Submission Form. Delivered the MXD6 10wt% AQ48 and MXD6 20wt% AQ48 to David Jessee for him to dry, but kept the other (Cobalt) Samples under N<sub>2</sub> flow Atmosphere.

The Following Materials were Submitted:

Item #	Reference for Center Layer	Center Layer Composition	Center Layer (Grams Submitted)	Outer Layer (Provided by B-125)
1	X26645-103-1	MXD6/D(ND)/Cobalt	500	9921
2	X26645-103-2	MXD6/D(ND)/SCPX-1578/Cobalt	500	9921
3	X26645-113-1	Amber PET 20261 4.0 wt% MXD6/D(ND)/Cobalt	1000	9921
4	X26645-113-2	Amber PET 20261 4.0 wt% MXD6/D(ND)/SCPX-1578/Cobalt	1000	9921
5	X26645-072-1	MXD6 10.0 wt% AQ48	1000	9921
6	X26645-072-2	MXD6 20.0 wt% AQ48	1000	9921

PPARL Processing Requests  
B125 DOOR EO

All requests must have a charge number

Submitter Linda Bernard Ext. 8060 Bldg. 150A Date [REDACTED]  
Project Name Beer Charge No. R.12582  
Polymer Type A Mixture of MXD6/D(ND)/COBALT/CLAY/PET 20216

Processing Machine  
David, if I did not indicate the correct machine, please use the machine you used when processing our previous samples. Linda

☒ Small Killion (Thin Film) ☐ Injection Molding (Preform)  
Screw General Purpose ☐ Mold  
☐ Large Killion (Thin Film) ☐ Reheat Blow (Bottles)  
Screw ☐ Free-blow (Bottles)  
☐ MPM (Thick Film or Sheet) ☐ Pipe Extrusion  
Screw ☐ Crystallizer  
☐ Blown Film ☐ Other

Polymer Drying Conditions: Temperature 120°C Time 24 Hours  
Flush Material 9921 for the extruder feeding the A Layers; MXD6 and PET 20261 for the extruder feeding Layer B  
Processing Temp: Melt 265°C Roll ☐ Mold  
Film: No. Layers 3 Thickness (See Note) Width ☐ Polished  
Disposition of Excess Resin Same as PET Film

\*MXD6/Cobalt and the MXD6/AQ48 Materials-We want Layer B to be 10 and 30% of the total thickness. The PET/MXD6/Cobalt materials-We want Layer B to be 10 and 50% of the total thickness.

#### Sample Description

Reference No. Instructions	Quantity	Comments / Special
X26645-117-1	500 to 600 grams	MXD6/D(ND)/COBALT
X26645-117-2	500 to 600 grams	MXD6/D(ND)/SCPX-1578/COBALT
X26645-117-3	1000 grams	AMBER PET 20261/MXD6/D(ND)/COBALT
X26645-117-4	1000 grams	AMBER PET 20261/MXD6/D(ND)/CLAY/COBALT
X26645-117-5	1000 grams	MXD6/AQ48
X26645-117-6	1000 grams	MXD6/AQ48

Submit request to David M. Jessee B125 (X-7373) U835201 FAX 6183

Processing Lab: Steve Darnell, Danny Glover, Mike Jones (X-5663)

David, I may be sending more of X26645-117-1 and 2 than what I listed, I am not sure how much I have. We want the B layer to be 10 and 30% of the total for -117-1, -117-2, -117-5 and -117-6; we want the B-layer to be 30 and 50% of the total thickness of -117-3 and -117-4. I wrote all this on the processing form, but just thought I would reiterate it. Thank you for taking care of this for us. I will carry the MXD6/AQ48 samples out there because I need to check with Danny Glover about a sample that we never received. Linda.

TEC 6573-3

SIGNATURE OF AUTHOR

Linda Bernard

DATE

SIGNATURE OF WITNESS

Patricia Williams

DATE

X 26645

No 123

Received Films (Tri-layer) That were Submitted on P-117 And  
Submitted them For ~~TM-Long Stretch~~, Etc.  
OPTICAL Measurements, 180° Peel

Objective: Have the film stretched and the PO<sub>2</sub>  
Tested to determine if the Cobalt and/or  
SCPX-1578 improves on O<sub>2</sub> Barrier. The  
AQ Samples are to be tested For improve-  
ment on adhesion.

Procedure: The 8 Samples Containing  
Cobalt were cut and placed in a  
bag that was then filled w/N<sub>2</sub> and  
Kept this way until Stretched. After  
Stretching I am requesting that  
they be put back under N<sub>2</sub> until  
they are placed on the Oxotran 220  
Cells to be tested For PO<sub>2</sub>.

Linda Bernard

Note: TM-Long Stretch and related data  
on P-124. lgb.

Item	Reference of Center Layer	Composition of Center Layer	Center Layer (Target Vol%)	Outer Layers	B-125 Reference of Tri Layer Films	180 Peel - low (gm/mm)	181 Peel - high (gm/mm)	Top Layer	Center Layer	Bottom Layer	Barrier (% Vol)
1	Lot 6007	MXD6	10	9921	X26736-052-0A	0.8/2	2.9/3	160	47	280	10
2	Lot 6007	MXD6	30	9921	X26736-052-0B	..	3.7/5	130	170	190	35
3	Lot 6007	MXD6	50	9921	X26736-052-0C	..	..	88	270	120	56
4	X26645-117-5	MXD6 10 w% AQ48	10	9921	X26736-054-5	1.0/5	..	160	63	270	13
5	X26645-117-5	MXD6 10 w% AQ48	30	9921	X26736-054-5	4.3/4	9.7/1	100	140	220	30
6	X26645-117-6	MXD6 20 w% AQ48	10	9921	X26736-054-6	0.8/5	..	130	63	290	13
7	X26645-117-6	MXD6 20 w% AQ48	30	9921	X26736-054-6	6.2/3	13.5/2	130	210	190	40
8	X26645-117-1	MXD6/D(ND)/Cobalt	10	9921	X26736-054-1	..	..	150	39	250	9
9	X26645-117-1	MXD6/D(ND)/Cobalt	30	9921	X26736-054-1	..	..	130	150	210	31
10	X26645-117-2	MXD6/D(ND)/SCPX-1578/Cobalt	10	9921	X26736-054-2	..	..	150	50	250	11
11	X26645-117-2	MXD6/D(ND)/SCPX-1578/Cobalt	30	9921	X26736-054-2	..	..	110	180	180	38
12	X26645-117-3	Amber PET 2061/MXD6/D(ND)/Cobalt	30	9921	X26736-054-3	..	..	99	130	200	30
13	X26645-117-3	Amber PET 2061/MXD6/D(ND)/Cobalt	50	9921	X26736-054-3	..	..	84	170	120	45
14	X26645-117-4	Amber PET 2061/MXD6/D(ND)/SCPX-1578/Cobalt	30	9921	X26736-054-4	..	..	130	140	190	40
15	X26645-117-4	Amber PET 2061/MXD6/D(ND)/SCPX-1578/Cobalt	50	9921	X26736-054-4	..	..	86	210	120	50

TEC 6573-3

SIGNATURE OF AUTHOR

Linda Bernard

DATE

SIGNATURE OF WITNESS

Shelton Wellman

DATE

No 124

X 26645

PEL Submission For Tri-Layer Film on P-123 For TM-Long Stretch, 180 Peel,  
Color + Haze

Polymers Evaluation Laboratory	
PEL Submission Form	
Submitter: LINDA BERNARD	Date: [REDACTED]
Insurance #: 792460	Charge/W.O. #: R12560
Building #: 150	VAX User ID: U792460
Phone #: 8060	Preassigned PEL #: [REDACTED]

• Project Category: 4	• Target Date: [REDACTED]
• Application: 4	• Project #: [REDACTED]
• Overtime is authorized to meet this target date: no	
Click on "Notebook #" item to enter the next material	
• X26645-123-1	• X26645-123-9
• X26645-123-2	• X26645-123-10
• X26645-123-3	• X26645-123-11
• X26645-123-4	• X26645-123-12
• X26645-123-5	• X26645-123-13
• X26645-123-6	• X26645-123-14
• X26645-123-7	• X26645-123-15
• X26645-123-8	Notebook #
• Hazards: no	
Submitter Pretreatments	Enter results into PDRS: no
• Testing ..	Return Excess Sample: yes

Film Checklist	Notebook Number	125-1	125-2	125-3	125-4	125-5	125-6	125-7	125-8	125-9	125-10	125-11	125-12	125-13	125-14	125-15
Acetabulide	Test Cond.															
Ash	Test Cond.															
Capillary Rheometer	Test Cond.															
Coef. of Friction	Test Cond.															
Density	Test Cond.															
Elmendorf Tear	Test Cond.															
Melt Flow Rate	Test Cond.															
CO <sub>2</sub> Permeability	Test Cond.															
Instrumented Impact	Test Cond.															
IV	Test Cond.															
O <sub>2</sub> Permeability	Test Cond.															
Refractive Index	Test Cond.															
Film Tear Force (D1938)	Test Cond.															
Film Heat Distortion Temperature	Test Cond.															
Film Tensile Properties (D882)	Test Cond.															
Thermal Analysis	Test Cond.															
T.M. Long Film Stretch	Test Cond.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Transparency	Test Cond.															
Water Vapor Permeability	Test Cond.															
180 Peel	Test Cond.	X	X													

Polymers Evaluation Laboratory	
T. M. Long Film Stretching Test Request	
• Stretch Temp (Deg. C): 105	Oriented Film Tests
• Stretch Temp (Deg. C):	
• Stretch Temp (Deg. C):	
• Stretch Ratios: 4X4	
• Stretch Ratios:	Film IUT:
• Tg (Deg. C): -83	CO <sub>2</sub> Permeability: * Test Cond.
• Stress Strain: yes	O <sub>2</sub> Permeability: * Test Cond.
• Machine: 4X	Film Tensile Properties:
• Number of Sheets: 3	Water Vapor Permeability:
• Stretch Rate: 14 in/sec	Color: * Test Cond.
• PSR (4X by 4X only and 14 in/sec): yes	Haze: Test Cond.
Previous Stretch conditions (if known)	
• Grip Pressure:	
• Soak Time: 60 SEC	
• Previous Stretch Temp (Deg. C):	
Comments RANDY, SAMPLES # 8 THROUGH 15 NEED TO BE KEPT UNDER NITROGEN AS MUCH AS POSSIBLE. I AM SENDING THEM TO YOU IN A BAG THAT HAS BEEN FILLED WITH N <sub>2</sub> . IF YOU WOULD PUT THEM IN A BAG AND FILL IT WITH N <sub>2</sub> AFTER STRETCHING I SURE WOULD APPRECIATE IT. THANK YOU! LINDA	

Item	Reference	Oxygen Permeability (cc mil/100"² 24-H atm)	Carbon Dioxide (Permeability) (cc CO <sub>2</sub> mil/100"² 24-H atm)	Carbon Dioxide (Transmission Rate) (cc CO <sub>2</sub> mil/100"² 24-H)	Haze (%)	L*	a*	b*	180 Peel low/#	180 Peel high/#	Top Layer (µm)	Center Layer (µm)	Bottom Layer (µm)	Barrier (% Vol)	PSR (Avg)
1	X26645-123-1	2.70	16.62	174.32	0.58	94.48	-0.77	-0.20	0.23	0.52	13.0	4.0	21.0	11	15.08
2	X26645-123-2	0.78	5.86	58.58	1.68	94.91	-0.87	-0.16	0.173	0.82	14.0	14.0	26.0	26	13.4
3	X26645-123-3	Would not stretch	Would not stretch	Would not stretch										#VALUE!	
4	X26645-123-4	5.52			32.92	94.37	-0.91	-0.19	did not peel	did not peel	11.3	5.6	24.0	14	15.01
5	X26645-123-5	1.12			44.64	94.66	-0.92	-0.06	did not peel	did not peel	12.5	16.5	28.5	30	14.41
6	X26645-123-6	3.41			6.54	94.69	-0.89	-0.15	did not peel	did not peel	12.3	4.9	21.7	13	15.08
7	X26645-123-7	4.79			40.52	94.69	-0.96	0.10	did not peel	did not peel	11.7	13.3	21.3	29	15.19
8	X26645-123-8	2.472/11	14.66	168.17	0.37	95.07	-0.89	-0.06	did not peel	did not peel	12.5	3.4	20.0	9	13.29
9	X26645-123-9	0.810/68	4.54	53.73	0.71	94.88	-0.91	0.04			11.0	9.4	18.3	24	14.44
10	X26645-123-10	1.931/84	10.88	117.47	0.79	94.98	-0.89	-0.06			12.3	3.6	21.3	10	12.65
11	X26645-123-11	0.690/51	3.91	40.76	2.33	94.73	-0.90	0.10			11.0	12.5	18.5	30	12.73
12	X26645-123-12	6.636/05	3.20	33.75	0.43	92.67	-0.80	10.41			11.0	9.5	22.0	22	13.13
13	X26645-123-13	6.516/13	25.17	410.73	0.43	92.06	-4.01	12.50			8.2	13.0	11.0	40	14.56
14	X26645-123-14	6.536/20	27.45	317.38	0.43	92.01	-3.96	12.46			9.0	11.0	15.0	31	13.43
15	X26645-123-15	5.925/66	22.98	290.93	0.39	91.3	-4.44	15.55			8.3	13.7	7.2	47	14.27

SIGNATURE OF AUTHOR

Linda Bernard

DATE

TEC 6573-4

SIGNATURE OF WITNESS

Dorinda Williams

DATE

X 26854

No 015

Sample	Clay	g of Clay	g Dried
Sample 1	x 26640-87	13.4	270
Sample 2	x 26640-85	13.2	269
Sample 3	x 26640-86	6.6	264

Extrusion on M-18 @ 275 rpm

temp profile

Zone 2 - 230°C

die pressure 20

Zone 3 240°C

melt T 236°C

Zone 4 240°C

Zone 5 240°C

Zone 6 245°C

Zone 7 245°C

Zone 8 250°C

die 250°C

TEC 6878-0

SIGNATURE OF AUTHOR

SIGNATURE OF WITNESS

DATE

DATE

X 26640

No

085

X-26640-85

This work is to prepare more of X26640-80

Suspend 2.36 g of cobalt(II)acetate tetrahydrate in 200 ml of water.

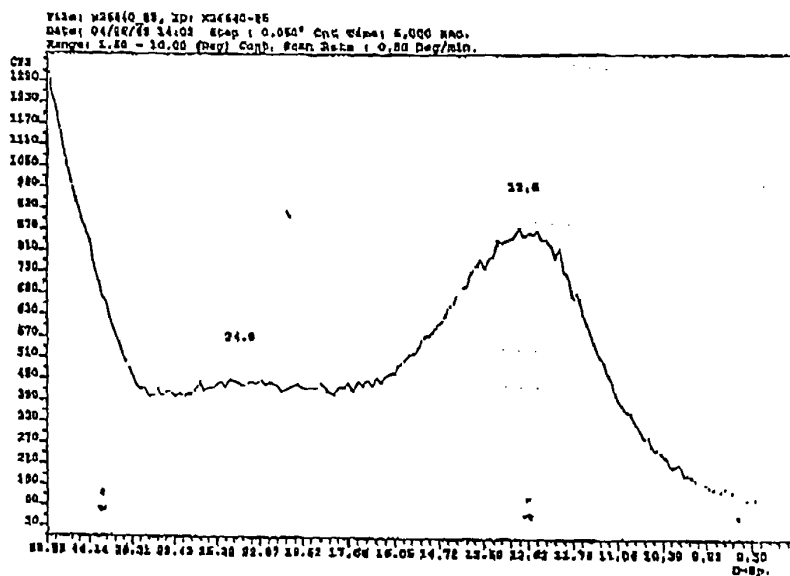
Suspend 40.0 g of SCPX-1276 in 2000 ml of hot water at 80 C in a Commercial Waring Blender and blend for two minutes.

Add the Cobalt solution to the Waring Blender and blend for two minutes.

Add <sup>50</sup> ml of 0.962 N HCl and blend for two minutes.

Centrifuge the mixture and pour off the water. Wash with 1000 ml of water in blender.

*[Handwritten signature]*



*[Handwritten: 1-2.4.0.20]*

*[Handwritten: 0/0]*

TED 66753

SIGNATURE OF AUTHOR

SIGNATURE OF WITNESS

DATE

DATE





X 26640

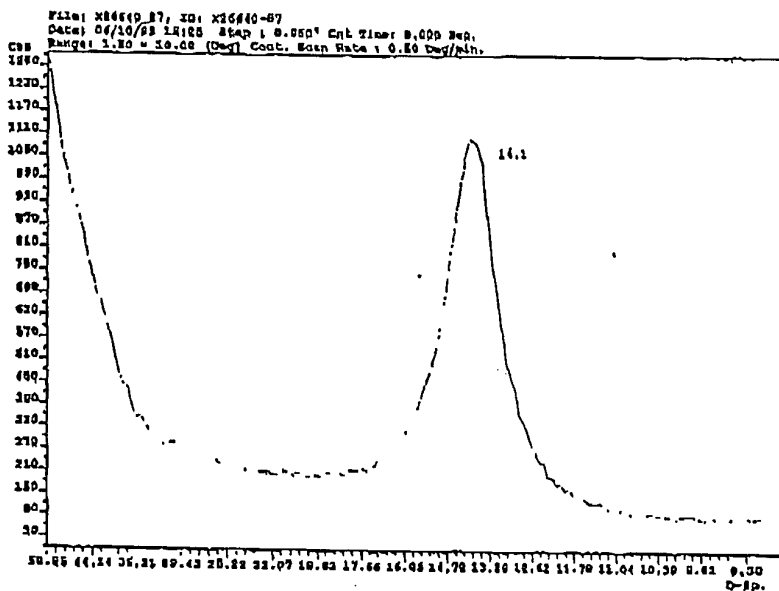
No 087

THIS WORK IS TO PREPARE AN ORGANOCLAY CONTAINING CO AND OCTADECYLTRIMETHYLAMMONIUM WITH A SOME SODIUM THAT WILL BE DISPLACED WITH H<sub>2</sub>O.

THIS CLAY SHOULD CONTAIN 47.5 MEG OF CO<sup>++</sup>, 23.75 MEG OF OCTADECYLTRIMETHYLAMMONIUM, AND 23.75 MEG AMINOPOLYANIDE.

SUSPEND 2.36 G (MW 249.08) OF COBALT II ACETATE TETRAHYDRATE AND 6.56 G OF ARQUAD 18-50 IN 300 ML OF WATER.

5  
2  
B  
A  
X  
B  
V



1276 in.  
AT 80°C  
AND  
LUTES.

OF  
END FOR

84.88%  
REMOVED  
A  
ASTED  
ER  
FREE

WAS DRIED  
OVEN

AT 60°C OVER NIGHT. COBALT = 1.14%  
% YIELD = 28.05 ME. SPIN = 7.5%

TED 8573-3 (2-68)

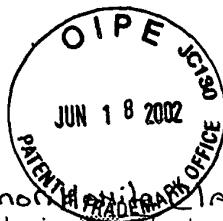
SIGNATURE OF AUTHOR

SIGNATURE OF WITNESS

DATE

DATE

No 122



X 25982

Properties of Montmorillonite Clays with Cobalt and H<sup>+</sup>

Table 1. MXD6 with Montmorillonite Clay Containing Co <sup>++</sup> and H <sup>+</sup>			
X26854-15- Composition	1		2
	Montmorillonite		Montmorillonite
	50% Co <sup>++</sup>	50% Co <sup>++</sup>	100% H <sup>+</sup>
	25% H <sup>+</sup>	50% H <sup>++</sup>	
	25% octadecyl trimethyl ammonium		
Ash	4.44	3.84	1.75
DSC (pellet)			
Tch1	203	88/199	209
Tm1	237	237	239
Tg	81	82	82
Tch2	133/198	134/198	139/200
Tm2	236	236	236
Tcc	181	181	178
WAXD Basal Spacing	none observed	1.4	1.38
WAXD Intensity	none observed	8633	2755
TEM Images	Tactoids	Tactoids	Tactoids

SIGNATURE OF AUTHOR

SIGNATURE OF WITNESS

*Jeffrey T. Owens*  
*Charles H. Henry*

DATE

DATE

TEC 6573-4

No 100

X 25982



(CONT. From Page 99)

Discussion of LCP and Clays / MXD6-Cobalt Ideas

Owens, Jeff

From: Gilmer, John W  
 To: Owens, Jeff  
 Subject: FW: OAT form

-----Original Message-----

From: Dawsey, Timothy R  
 To: Gilmer, John W  
 Subject: FW: OAT form

-----Original Message-----

From: FrontPage.Email.Form@eastman.com [SMTP:FrontPage.Email.Form@eastman.com]  
 To: u836177%ntmcon02.emn.com.u856790%ntmcon02.emn.com.u790667%ntmcon02.emn.com.u858447%  
 ntmcon02.emn.com.u791425%ntmcon02.emn.com.u791320@eastman.com : : : : :  
 Subject: OAT form

\*\*\*\*\*  
 BO Requested: NBO, CPBO, SPBO  
 Username: Jeff Owens  
 UserTel: 7328  
 Contact: [REDACTED]

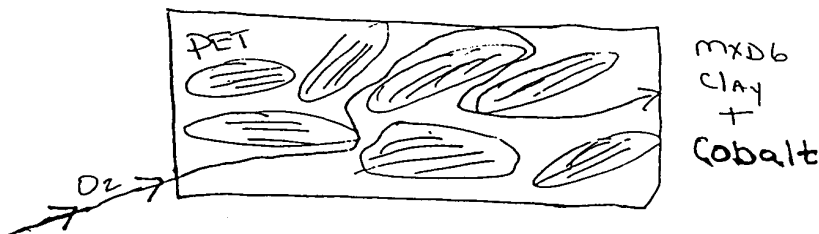
Time: 11:02:11 AM  
 Remote User: EASTMAN\U857191

## Comments:

I recently read an article showing Oxygen permeability vs. Water vapor data for several resins these included PET, Nylon and LCP. LCP was by far the most superior with respect to permeability. I am sure there is data on PET/LCP blends but I thought the idea of put clay in LCP and making a trilayer film in PET would be interesting since we produce LCP we could buy it at our cost which might be cheaper than buying MXD6 Nylon.

## Idea on Combining MXD6 Nylon with clay and Cobalt

I discussed with Dr. Chris Matayabas the idea of using the combination high barrier MXD6 nanocomposite with oxygen scavenging of Cobalt in the polymer matrix. In theory the O<sub>2</sub> molecules that flowed thru the nanocomposite would be cleaved by the Cobalt thus providing a material with better barrier potential in the market place with respect the beer.



(CONT. TO PAGE 123)

SIGNATURE OF AUTHOR

Jeffrey T. Owens  
 Samuel D. Hilbert

DATE

SIGNATURE OF WITNESS

DATE

TEC 6573-4

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of:

Bernard et al.

Serial No.: 09/630,517

Filed: August 02, 2000

For: POLYAMIDE NANOCOMPOSITES WITH OXYGEN SCAVENGING  
CAPABILITY

Group Art Unit: 1714

Examiner: K. I. Wyrozebski Lee

Commissioner of Patents and Trademarks  
Washington, D.C. 20231DECLARATION UNDER 37 CFR 1.131

We, Linda G. Bernard, Horst Clauberg, Michael J. Cyr, John W. Gilmer, James C. Matayabas, Jr., Jeffery T. Owens, Mark E. Stewart, Sam R. Turner, and Shriram Bagrodia declare that:

1. We are the coinventors of claims 1-29 of the above-identified patent application.
2. Prior to August 5, 1999, having earlier conceived the idea of recyclable polymer nanocomposite with improved oxygen and gas barrier properties comprising at least one polyamide resin, at least one oxygen-scavenging catalyst, and at least one layered silicate material, Linda G. Bernard, Jeffrey T. Owens, Marvin C. Hagey, and John W. Gilmer prepared the following polyamide polymer compositions, described herein, at the Research Laboratories of Eastman Chemical Co., Kingsport, Tennessee.
  - A) The following general procedures were used to measure oxygen consumption and carbon dioxide permeability. Oxygen consumption was measured on film samples, which were cut into strips, using a Columbus Instruments Micro-Oxymax respirometer with version 6.04b software. Samples were placed into a glass media bottle with a nominal volume of 250 mL. One empty bottle was included as a control blank. The bottles were attached to a ten port expansion module. Readings were taken at the start of the experiment and

then every four hours. The instrument measured the change in the oxygen concentration from the previous reading in each cell and calculated the total oxygen consumption and rate based on the (previously measured) volume of the cell plus oxygen sensor system. The oxygen sensor is an electrochemical fuel cell. Carbon dioxide transmission rates were measured on film samples using a Mocon permeability analyzer.

- B) An unmodified MXD6 polyamide was prepared by extruding two trilayer films comprising internal layers of about 10 and 30 vol% of unmodified MXD6 6007, available from Mitsubishi Gas Company, with two external layers of PET-9921, available from Eastman Chemical Company. Several 2-inch square sections of the trilayer films were stretched using a T. M. Long instrument (4x4 orientation at about 110°C). The carbon dioxide transmission rates were 174 and 59 cc(STP) CO<sub>2</sub>/meter<sup>2</sup>/24hr, for the 10 and 30 vol% films respectively.

A MXD6 polyamide composition containing about 4000 ppm cobalt acetate as an oxygen-scavenging catalyst was prepared by mixing 250 grams of a low molecular weight, amine terminated poly(m-xylylene adipamide), with IV of about 0.44 dL/g, and 4.23 grams of cobalt acetate tetrahydrate under a nitrogen atmosphere at 250°C for 120 minutes then cooling. X-ray analysis of the product showed the concentration of cobalt in the product to be about 4000 ppm. This cobalt-containing polyamide (10 parts) was extrusion compounded with 90 parts of MXD6 6007, available from Mitsubishi Gas Company, at 250°C, to give material with a cobalt concentration about 400 ppm. The polyamide was used to prepare trilayer films and 2-inch square sections of the films were stretched as described above. The carbon dioxide transmission rates of the oriented films were determined to be 168 and 54 cc(STP) CO<sub>2</sub>/meter<sup>2</sup>/24hr, for the 10 and 30 vol% films respectively. Oxygen consumption for 3.0 grams of the inner polyamide layer, after removing the PET 9921 layers from the unoriented film comprising 30 vol% polyamide, was determined to be about 370 microliters of oxygen over a period of 136 hours.

C) Using the procedure of example B, an MXD6 polyamide composition containing a layered silicate material and cobalt as an oxygen-scavenging catalyst was prepared by mixing 215.75 grams of a low molecular weight, amine terminated poly(m-xylylene adipamide), with IV of about 0.44 dL/g, 34.25 grams of SCPX-1578, an organoclay available from Southern Clay Products, and 4.23 grams of cobalt(II) acetate tetrahydrate under a nitrogen atmosphere at 250°C for 120 minutes followed by cooling. Ten parts of this product was extrusion compounded with 90 parts of MXD6 6007, available from Mitsubishi Gas Company at about 260°C to give material with a cobalt concentration of about 400 ppm and silicate concentration (ash) of about 1.0 wt%.

Two trilayer films were extruded comprising internal layers of about 10 and 30 vol% of the above compounded MXD6 6007 with two external layers of PET-9921, available from Eastman Chemical Company. Trilayer films were prepared and oriented as described above. The carbon dioxide transmission rates for the oriented films were 117 and 41 cc(STP) CO<sub>2</sub>/meter<sup>2</sup>/24hr, for the 10 and 30 vol% films respectively. Oxygen consumption for 3.0 grams of the inner nanocomposite layer, after removing the PET 9921 layers from the unoriented film comprising 30 vol% nanocomposite, was determined to be about 680 microliters of oxygen over a period of 136 hours.

D) Another MXD6 polyamide composition containing an oxygen-scavenging catalyst was prepared in which 4 parts of the MXD6 composite prepared in example B was extrusion compounded with 96 parts of amber PET-20261, available from Eastman Chemical Company. A trilayer film was extruded comprising internal layers of about 50 vol% of this material with two external layers of PET-9921, available from Eastman Chemical Company. Several 2-inch square sections of the trilayer films were prepared and oriented as above. The carbon dioxide transmissions rate of the oriented films were 411 cc(STP) CO<sub>2</sub>/meter<sup>2</sup>/24hr, for the 50 vol% films. Oxygen consumption for 10

grams of the unoriented film comprising 50 vol% of the extrudate of PET 9921 with the PET-polyamide composite was determined to be about 60 microliters of oxygen over a period of 136 hours.

- E) Another MXD6 polyamide composition containing a layered silicate material and an oxygen-scavenging catalyst was prepared in which 4 parts of the MXD6 composite prepared in example C was extrusion compounded with 96 parts of amber PET-20261, available from Eastman Chemical Company. Two trilayer films were extruded comprising internal layers of about 30 and 50 vol% of this material with two external layers of PET-9921, available from Eastman Chemical Company. Trilayer films were prepared and oriented as above. The carbon dioxide transmissions rates of the oriented films were determined to be 317 and 291 cc(STP) CO<sub>2</sub>/meter<sup>2</sup>/24hr, for the 30 and 50 vol% films respectively. Oxygen consumption for 10 grams of the unoriented film comprising 50 vol% of the extrudate of PET 9921 with the nanocomposite was determined to be about 60 microliters of oxygen over a period of 136 hours.
- F) A polyamide composition was prepared in which the oxygen-scavenging catalyst, cobalt, was intercalated into the polymer matrix through the layered silicate material. A Wyoming-type montmorillonite clay was prepared in which 50% of the sodium cations were exchanged with cobalt and 50% with protons. Ash content of the clay was 87.15 wt %, cobalt content was 1.23 %, and X-ray basal spacing was 1.25 nm. The treated clay was dry mixed with 269 parts of a low molecular weight poly(m-xylylene adipamide), with IV of about 0.41 dL/g. The mixture was dried at 110°C overnight in a vacuum oven then extruded. The extruded material showed good oxygen consumption.
- G) Another polyamide composition was prepared identically to E except the montmorillonite clay used in the composition had 50 % of the sodium cations are exchanged with cobalt(II), 25% with octadecyltrimethylammonium cations,

and 25 % with protons. The clay had a cobalt content of 0.99 %, and X-ray basal spacing of 1.34 nm. The extruded material showed good oxygen consumption.

3. Evidence supporting the above examples above are provided by copies of research notebook pages as set forth in the table below and attached hereto:

Experiment	Supporting Notebook Pages	Performed by
B	X-26645-100 X-26645-103 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
C	X-26645-101 X-26645-103 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
D	X-26645-103 X-26645-113 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
E	X-26645-101 X-26645-103 X-26645-113 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
F	X-26640-085 X-26854-015 X-25982-122	Marvin C. Hagey John W. Gilmer Jeffery T. Owens
G	X-26640-087 X-26854-015 X-25982-122	Marvin C. Hagey John W. Gilmer Jeffery T. Owen



Further evidence of the conception of one aspect of this invention is provided by page X-25982-100 from Mr. Owens notebook, also attached hereto.

4. Each of the dates deleted from the attached notebook pages is prior to August 5, 1999.

The undersigned declares further that all statements made herein on his own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with a knowledge that willful, false statements, and the like so made are punishable by fine, or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

\_\_\_\_\_  
Date

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Date

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Date

\_\_\_\_\_  
Linda Gail Bernard

\_\_\_\_\_  
Horst Clauberg

\_\_\_\_\_  
Michael John Cyr

\_\_\_\_\_  
John Walker Gilmer

\_\_\_\_\_  
James Christopher Matayabas, Jr.

\_\_\_\_\_  
Jeffery Todd Owens

\_\_\_\_\_  
Mark Edward Stewart

\_\_\_\_\_  
Sam Richard Turner

Docket: 71111

PATENT

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Date

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Shriram Bagrodia

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of:

Bernard et al.

Serial No.: 09/630,517

Group Art Unit: 1714

Filed: August 02, 2000

Examiner: K. I. Wyrozebski Lee

For: POLYAMIDE NANOCOMPOSITES WITH OXYGEN SCAVENGING  
CAPABILITYCommissioner of Patents and Trademarks  
Washington, D.C. 20231DECLARATION UNDER 37 CFR 1.131

We, Linda G. Bernard, Horst Clauberg, Michael J. Cyr, John W. Gilmer, James C. Matayabas, Jr., Jeffery T. Owens, Mark E. Stewart, Sam R. Turner, and Shriram Bagrodia declare that:

1. We are the coinventors of claims 1-29 of the above-identified patent application.
2. Prior to August 5, 1999, having earlier conceived the idea of recyclable polymer nanocomposite with improved oxygen and gas barrier properties comprising at least one polyamide resin, at least one oxygen-scavenging catalyst, and at least one layered silicate material, Linda G. Bernard, Jeffrey T. Owens, Marvin C. Hagey, and John W. Gilmer prepared the following polyamide polymer compositions, described herein, at the Research Laboratories of Eastman Chemical Co., Kingsport, Tennessee.
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*use 6/5/02*

then every four hours. The instrument measured the change in the oxygen concentration from the previous reading in each cell and calculated the total oxygen consumption and rate based on the (previously measured) volume of the cell plus oxygen sensor system. The oxygen sensor is an electrochemical fuel cell. Carbon dioxide transmission rates were measured on film samples using a Mocon permeability analyzer.

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msc 6/5/02

- C) Using the procedure of example B, an MXD6 polyamide composition containing a layered silicate material and cobalt as an oxygen-scavenging catalyst was prepared by mixing 215.75 grams of a low molecular weight, amine terminated poly(m-xylylene adipamide), with IV of about 0.44 dL/g, 34.25 grams of SCPX-1578, an organoclay available from Southern Clay Products, and 4.23 grams of cobalt(II) acetate tetrahydrate under a nitrogen atmosphere at 250°C for 120 minutes followed by cooling. Ten parts of this product was extrusion compounded with 90 parts of MXD6 6007, available from Mitsubishi Gas Company at about 260°C to give material with a cobalt concentration of about 400 ppm and silicate concentration (ash) of about 1.0 wt%.

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- G) Another polyamide composition was prepared identically to E except the montmorillonite clay used in the composition had 50 % of the sodium cations are exchanged with cobalt(II), 25% with octadecyltrimethylammonium cations,

and 25 % with protons. The clay had a cobalt content of 0.99 %, and X-ray basal spacing of 1.34 nm. The extruded material showed good oxygen consumption.

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Experiment	Supporting Notebook Pages	Performed by
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C	X-26645-101 X-26645-103 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
D	X-26645-103 X-26645-113 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
E	X-26645-101 X-26645-103 X-26645-113 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
F	X-26640-085 X-26854-015 X-25982-122	Marvin C. Hagey John W. Gilmer Jeffery T. Owens
G	X-26640-087 X-26854-015 X-25982-122	Marvin C. Hagey John W. Gilmer Jeffery T. Owen

*max 6/5/02*

Further evidence of the conception of one aspect of this invention is provided by page X-25982-100 from Mr. Owens notebook, also attached hereto.

4. Each of the dates deleted from the attached notebook pages is prior to August 5, 1999.

The undersigned declares further that all statements made herein on his own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with a knowledge that willful, false statements, and the like so made are punishable by fine, or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Date

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Linda Gail Bernard

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Date

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Horst Clauberg

June 5, 2002  
Date

Michael John Cyr  
Michael John Cyr

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Date

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John Walker Gilmer

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Date

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James Christopher Matayabas, Jr.

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Jeffery Todd Owens

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Date

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Mark Edward Stewart

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Date

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Sam Richard Turner



Docket: 71111

PATENT

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Date

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Shriram Bagrodia

*msl 6/5/02*



**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of:

Bernard et al.

Serial No.: 09/630,517

Group Art Unit: 1714

Filed: August 02, 2000

Examiner: K. I. Wyrozebski Lee

For: POLYAMIDE NANOCOMPOSITES WITH OXYGEN SCAVENGING  
CAPABILITY

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**DECLARATION UNDER 37 CFR 1.131**

We, Linda G. Bernard, Horst Clauberg, Michael J. Cyr, John W. Gilmer, James C. Matayabas, Jr., Jeffery T. Owens, Mark E. Stewart, Sam R. Turner, and Shriram Bagrodia declare that:

1. We are the coinventors of claims 1-29 of the above-identified patent application.
2. Prior to August 5, 1999, having earlier conceived the idea of recyclable polymer nanocomposite with improved oxygen and gas barrier properties comprising at least one polyamide resin, at least one oxygen-scavenging catalyst, and at least one layered silicate material, Linda G. Bernard, Jeffrey T. Owens, Marvin C. Hagey, and John W. Gilmer prepared the following polyamide polymer compositions, described herein, at the Research Laboratories of Eastman Chemical Co., Kingsport, Tennessee.

A) The following general procedures were used to measure oxygen consumption and carbon dioxide permeability. Oxygen consumption was measured on film samples, which were cut into strips, using a Columbus Instruments Micro-Oxymax respirometer with version 6.04b software. Samples were placed into a glass media bottle with a nominal volume of 250 mL. One empty bottle was included as a control blank. The bottles were attached to a ten port expansion module. Readings were taken at the start of the experiment and

then every four hours. The instrument measured the change in the oxygen concentration from the previous reading in each cell and calculated the total oxygen consumption and rate based on the (previously measured) volume of the cell plus oxygen sensor system. The oxygen sensor is an electrochemical fuel cell. Carbon dioxide transmission rates were measured on film samples using a Mocon permeability analyzer.

- B) An unmodified MXD6 polyamide was prepared by extruding two trilayer films comprising internal layers of about 10 and 30 vol% of unmodified MXD6 6007, available from Mitsubishi Gas Company, with two external layers of PET-9921, available from Eastman Chemical Company. Several 2-inch square sections of the trilayer films were stretched using a T. M. Long instrument (4x4 orientation at about 110°C). The carbon dioxide transmission rates were 174 and 59 cc(STP) CO<sub>2</sub>/meter<sup>2</sup>/24hr, for the 10 and 30 vol% films respectively.

A MXD6 polyamide composition containing about 4000 ppm cobalt acetate as an oxygen-scavenging catalyst was prepared by mixing 250 grams of a low molecular weight, amine terminated poly(m-xylylene adipamide), with IV of about 0.44 dL/g, and 4.23 grams of cobalt acetate tetrahydrate under a nitrogen atmosphere at 250°C for 120 minutes then cooling. X-ray analysis of the product showed the concentration of cobalt in the product to be about 4000 ppm. This cobalt-containing polyamide (10 parts) was extrusion compounded with 90 parts of MXD6 6007, available from Mitsubishi Gas Company, at 250°C, to give material with a cobalt concentration about 400 ppm. The polyamide was used to prepare trilayer films and 2-inch square sections of the films were stretched as described above. The carbon dioxide transmission rates of the oriented films were determined to be 168 and 54 cc(STP) CO<sub>2</sub>/meter<sup>2</sup>/24hr, for the 10 and 30 vol% films respectively. Oxygen consumption for 3.0 grams of the inner polyamide layer, after removing the PET 9921 layers from the unoriented film comprising 30 vol% polyamide, was determined to be about 370 microliters of oxygen over a period of 136 hours.

- C) Using the procedure of example B, an MXD6 polyamide composition containing a layered silicate material and cobalt as an oxygen-scavenging catalyst was prepared by mixing 215.75 grams of a low molecular weight, amine terminated poly(m-xylylene adipamide), with IV of about 0.44 dL/g, 34.25 grams of SCPX-1578, an organoclay available from Southern Clay Products, and 4.23 grams of cobalt(II) acetate tetrahydrate under a nitrogen atmosphere at 250°C for 120 minutes followed by cooling. Ten parts of this product was extrusion compounded with 90 parts of MXD6 6007, available from Mitsubishi Gas Company at about 260°C to give material with a cobalt concentration of about 400 ppm and silicate concentration (ash) of about 1.0 wt%.

Two trilayer films were extruded comprising internal layers of about 10 and 30 vol% of the above compounded MXD6 6007 with two external layers of PET-9921, available from Eastman Chemical Company. Trilayer films were prepared and oriented as described above. The carbon dioxide transmission rates for the oriented films were 117 and 41 cc(STP) CO<sub>2</sub>/meter<sup>2</sup>/24hr, for the 10 and 30 vol% films respectively. Oxygen consumption for 3.0 grams of the inner nanocomposite layer, after removing the PET 9921 layers from the unoriented film comprising 30 vol% nanocomposite, was determined to be about 680 microliters of oxygen over a period of 136 hours.

- D) Another MXD6 polyamide composition containing an oxygen-scavenging catalyst was prepared in which 4 parts of the MXD6 composite prepared in example B was extrusion compounded with 96 parts of amber PET-20261, available from Eastman Chemical Company. A trilayer film was extruded comprising internal layers of about 50 vol% of this material with two external layers of PET-9921, available from Eastman Chemical Company. Several 2-inch square sections of the trilayer films were prepared and oriented as above. The carbon dioxide transmissions rate of the oriented films were 411 cc(STP) CO<sub>2</sub>/meter<sup>2</sup>/24hr, for the 50 vol% films. Oxygen consumption for 10

grams of the unoriented film comprising 50 vol% of the extrudate of PET 9921 with the PET-polyamide composite was determined to be about 60 microliters of oxygen over a period of 136 hours.

- E) Another MXD6 polyamide composition containing a layered silicate material and an oxygen-scavenging catalyst was prepared in which 4 parts of the MXD6 composite prepared in example C was extrusion compounded with 96 parts of amber PET-20261, available from Eastman Chemical Company. Two trilayer films were extruded comprising internal layers of about 30 and 50 vol% of this material with two external layers of PET-9921, available from Eastman Chemical Company. Trilayer films were prepared and oriented as above. The carbon dioxide transmissions rates of the oriented films were determined to be 317 and 291 cc(STP) CO<sub>2</sub>/meter<sup>2</sup>/24hr, for the 30 and 50 vol% films respectively. Oxygen consumption for 10 grams of the unoriented film comprising 50 vol% of the extrudate of PET 9921 with the nanocomposite was determined to be about 60 microliters of oxygen over a period of 136 hours.
- F) A polyamide composition was prepared in which the oxygen-scavenging catalyst, cobalt, was intercalated into the polymer matrix through the layered silicate material. A Wyoming-type montmorillonite clay was prepared in which 50% of the sodium cations were exchanged with cobalt and 50% with protons. Ash content of the clay was 87.15 wt %, cobalt content was 1.23 %, and X-ray basal spacing was 1.25 nm. The treated clay was dry mixed with 269 parts of a low molecular weight poly(m-xylylene adipamide), with IV of about 0.41 dL/g. The mixture was dried at 110°C overnight in a vacuum oven then extruded. The extruded material showed good oxygen consumption.
- G) Another polyamide composition was prepared identically to E except the montmorillonite clay used in the composition had 50 % of the sodium cations are exchanged with cobalt(II), 25% with octadecyltrimethylammonium cations,

and 25 % with protons. The clay had a cobalt content of 0.99 %, and X-ray basal spacing of 1.34 nm. The extruded material showed good oxygen consumption.

3. Evidence supporting the above examples above are provided by copies of research notebook pages as set forth in the table below and attached hereto:

Experiment	Supporting Notebook Pages	Performed by
B	X-26645-100 X-26645-103 X-26645-117 X-26645-123 X-26645-124	Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard Linda G. Bernard
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The undersigned declares further that all statements made herein on his own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with a knowledge that willful, false statements, and the like so made are punishable by fine, or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Linda Gail Bernard

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Horst Clauberg

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Date

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Michael John Cyr

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Date

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John Walker Gilmer

\_\_\_\_\_  
Date

*6/3/2002*

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*James Christopher Matayabas, Jr.*  
James Christopher Matayabas, Jr.

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Date

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Jeffery Todd Owens

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Date

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Mark Edward Stewart

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Date

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Sam Richard Turner

Docket: 71111

PATENT

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Date

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Shriram Bagrodia